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New Bedford Harbor Pilot Study

Pre-operational Monitoring - Progress Report:

Chemical Analysis Results From the Two Pre-operational
Water Samplings Conducted in New Bedford Harbor During
July 1987

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INTRODUCTION

Seawater sampling for chemical analysis was done at four stations in New Bedford Harbor on July 9th and July 13th of 1987. Composite samples from ebb and flood tides were obtained on each day and analyzed for polychlorinated biphenyls (PCBs), copper (Cu), cadmium (Cd) and lead (Pb).

On July 9 samples were collected at stations 1,3 and 4 once per hour for 5 hours during the ebb and flood tides. These samples were composited and analyzed for whole water PCBs, Cu, Cd and Pb. At station 2, a composite sample for whole water analysis was collected as indicated above. In addition, each hour aliquots were filtered and the filters and filtrates (samples were filtered separately for PCB and trace metal analysis) were composited. On July 13, 1987 whole water, dissolved and particulate composite samples were collected from each station and tidal cycle in the same manner as described above. These samples were all analyzed for PCBs, Cu, Cd and Pb.

METHODS AND MATERIALS

PCB Analyses

Two hundred ml of seawater were collected five times during each tidal cycle from each station. The five aliquots from each station over a tidal cycle were composited for a whole water sample. Additional samples from some stations and dates were filtered. The filters and filtrates were analyzed as a measure of the particulate and dissolved PCB concentrations.

Whole water and dissolved phase samples were extracted three times with 50 ml of freon. The extracts are combined, treated with sodium sulfate and then volume reduced. Volume reduction was done using a heating mantle and a Kuderna-Danish evaporator with a 3-ball Snyder column. The extract was volume reduced and solvent exchanged to about 10 ml of hexane. The sample was transferred to a concentrator tube fitted with a micro-Snyder column, then reduced and exchanged to 1 ml of heptane. The extract was partitioned against concentrated sulfuric acid and stored in a screw-top vial prior to instrumental analysis.

Filter samples were extracted two times with acetone and once with freon (25 ml each time) using a Polytron homogenizer. After each extraction the sample was centrifuged and the supernatant decanted into a 1 liter separatory funnel containing deionized water. The funnel shaken, and the freon layer drawn off into an Erlenmeyer flask. This partitioning was repeated 2 more times using 25 ml of freon each time and the extracts combined and treated with sodium sulfate. All freon extracts were then volume reduced and solvent exchanged to 1 ml of heptane as described above and treated with sulfuric acid.

The samples were analyzed for PCBs by capillary gas chromatography (GC). For these analyses, 1 ul of each sample was injected splitless into a Hewlett Packard 5890 gas chromatograph

equipped with a 30 m DB-5 fused silica capillary column (J + W Scientific) and an electron capture detector. Helium was used as the carrier gas at a flow rate of about 1.5 ml/min and the flow of a 95:5 mixture of argon:methane to the detector was 35 ml/min. The oven temperature was held at 60 C for 1 min and then programmed from 60 to 315 C at 10 C/min. The injector temperature was 270 C, and the detector was maintained at 325 C. Analog data from the gas chromatographs was digitized using a Perkin Elmer LCI-100 integrator interfaced to a Perkin Elmer LIMS/CLAS system for the quantification of PCB congeners. The results were stored on the Perkin Elmer LIMS systems and after QA were shipped to the laboratory VAX computer system.

The concentrations of Aroclors 1242 and 1254 were quantified. These two mixtures were the predominant Aroclors found in New Bedford Harbor samples. Two peaks from each of these Aroclor mixtures were used for quantification. The peaks chosen included two early eluting peaks from A1242 and two late eluting peaks from A1254. The peaks used for each of the Aroclors were not found (or were very minor) in the other Aroclor mixture. Therefore, the concentrations of the two Aroclors can be added as a measure of total PCBs without overestimating the concentrations due to overlapping peaks found in the two Aroclor mixtures. In addition, thirteen individual PCB congeners were quantified. These included at least one compound from each chlorination level ranging from tetrachlorobiphenyls to decachlorobiphenyl.

Inorganic Analyses - Cadmium, Lead and Copper

Fifty ml seawater samples were collected for inorganic analysis five times during each tidal cycle and these were composited. The samples to be filtered were passed through a Nucleopore filter after each collection and the filters and filtrates from each tidal cycle were combined separately. After collection all of the water samples for inorganic analysis were acidified to pH 2 for storage. The three sample types (whole water, particulate and dissolved) were analyzed using the methods described below.

Whole water - For whole water analyses, a 1 ml aliquot of each sample was taken and acidified with 100 ul of ultra-pure nitric acid. Standards were prepared in trace metal stripped seawater that was acidified with the same acid.

Particulate - The Nucleopore filters were acidified with 5 ml of 2 N nitric acid and ultrasonicated for 1 hr. Standards were prepared in the same 2 N HNO₃. Stripped seawater was added to both samples and standards to minimize variation in the sample matrix.

Dissolved - The dissolved samples were preconcentrated prior to analysis using the APDC-Co precipitation technique first described by Boyle and Edmund (1975) including several later modifications. This method results in an approximate 50-fold concentration factor.

All analyses were run on a Perkin-Elmer 5000 atomic absorption spectrophotometer (AA) equipped with an HGA 500 graphite furnace with Zeeman background correction and AS40 autosampler. The instrument conditions for HGA-AA determinations were similar to those described

in "Methods for Chemical Analysis of Water and Wastes" (U.S. EPA, 1979) and in the manufacturer's reference manuals. The AA instrument was calibrated each time samples were analyzed for a given element. Data from the AA was processed on a Perkin Elmer 3600 computer and then sent to the LIMS system.

RESULTS AND DISCUSSION

PCBs

The PCB results for samples collected on July 9, 1987 are shown in Table 1. Composited whole water samples from the ebb and flood tides were analyzed from each of the four stations. The samples were analyzed for PCBs as Aroclors 1242 and 1254 and these concentrations were summed as a measure of Total PCBs. There were differences in the concentrations between the ebb and flood tides; however, there were no consistent differences at all of the four stations.

A simple mean was taken of the values measured on the two tides at each station. This was done to allow an easier comparison of the concentrations reported at the four stations. These data show that the levels decrease from 0.758 at Station 1 to 0.102 at Station 4.

On July 13, samples were again collected five times during both the ebb and flood tides at each of the four stations. All of the samples collected on this date were filtered and PCB concentrations were measured on both the dissolved and particulate phases. The results from these analyses are shown in Table 2. The dissolved and particulate phase concentrations were added and this information is provided in the column labeled 'Sum'. A simple mean of the summed Total PCB concentrations is also provided to allow easy comparisons of the levels found at the four stations. As was found on July 9, the concentrations decreased from Station 1 to Station 4. The trends and mean PCB levels measured on the two sampling dates were very similar. This can be seen in Figure 1 which is a plot of the mean data from each tide on the two dates.

Some additional analyses were also conducted on the dissolved and particulate phases of the seawater samples collected from Station 2 on July 9. Table 3 shows a comparison of results with similar samples collected on July 13. The results indicate that the levels and distributions of PCBs at Station 2 were very similar on the two dates.

On July 13, both whole water and dissolved and particulate phase samples were collected from Station 2. This allowed a comparison of whole water concentrations with the sum of dissolved and particulate phase concentrations. These comparisons are shown in Table 4. The results indicate that the levels measured from the sum of the dissolved and particulate phase concentrations are similar to the measured whole water levels.

The concentrations of thirteen individual PCB congeners were also measured in all of the samples that were analyzed. A listing of the congeners quantified is provided in Table 5. The levels of each of the compounds in the samples collected on July 9 are shown in Table 6. The data for these compounds in the July 13 samples can be found in

Table 6. These data will provide important information of the partitioning of compounds with known n-octanol/water partition coefficients. Such discussions are, however, beyond the scope of this report.

Trace Metals

Tables 8 and 9 contain results of the inorganic analyses conducted on samples collected from New Bedford Harbor on July 9th and July 13th respectively. Results are given in ug/l for the whole water, particulate and dissolved samples.

Cadmium

Whole water cadmium concentrations at the four stations ranged from 0.06 to 0.34 ug/l. Concentrations tended to be lowest at Station 4, the station near the Hurricane barrier. Otherwise no obvious trends were apparent between stations or between ebb and flood tides. In the samples that were analyzed for dissolved and particulate Cd, there was very little variation in the dissolved levels, 0.10 to 0.19 ug/l. Greater variation was found in the particulate concentrations, 0.005 to 0.051 ug/l and there was a consistent decrease from station 1 to station 4 the furthest down bay on both ebb and flood tides. Cadmium is usually found predominantly in the dissolved fraction in marine systems and that is generally the case here although there is as much as 32 % particulate at the upper stations and as low as 5 % at Station 4. All results were well below the U.S. EPA Marine Water Quality Criteria level of 43 ug/l for cadmium.

Lead

As with cadmium, the whole water concentrations of lead did not show much variability, ranging from 2.4 to 4.2 ug/l with the lowest concentrations appearing at station 4. Lead is generally found primarily in the particulate fraction however here the particulate fraction is only about 50 % of the sum of the dissolved and particulate concentrations (43-63 %). There does not seem to be a major difference between stations or between tides for either particulate or soluble lead although like cadmium, the particulate concentrations decreased from Station 1 to Station 4 and all results were well below the U.S. EPA Marine Water Quality Criteria of 140 ug/l.

Copper

Copper concentrations showed the most variability, ranging from 1.6 to 11.8 ug/l for the whole water samples. The lowest concentrations were found at Station 4 and the highest were found at Station 3. This pattern was consistent for both days and for both ebb and flood tide. Fifty to 63 % of the copper at Stations 1 to 3 was in the particulate fraction while at station 4 this ranged from 30 to 40 %. Typically particulate copper is less than 50 % of the total concentration. The U.S. EPA Marine Water Quality Criteria for copper

is 2.9 ug/l and this is consistently exceeded at the upper three stations.

CONCLUSIONS

In summary, PCB concentrations measured as both Aroclor 1242 and Aroclor 1254 were found in seawater samples from New Bedford Harbor. PCBs were found in both the dissolved and particulate phases of the samples. The measured concentrations were highest at Station 1 (north of the Coggeshal Street Bridge) and decreased with distance downbay.

The PCB concentrations measured at the Hurricane Barrier (Station 4) were about 0.1 ug/g. Although these levels were the lowest found in this study, the concentrations measured at this site are considerably elevated compared to 'background' levels in the marine environment. For example, de Lappe et al. (1980) reported that PCB concentrations in seawater samples from 'relatively clean' areas of Buzzards Bay and off of Cape Cod ranged from 0.001 to 0.003 ug/l. This indicates that the PCB levels in New Bedford Harbor are greatly elevated as far south as the Hurricane Barrier. All of the samples analyzed in this study contained PCB levels above the U.S. EPA Marine Water Quality Criteria of 0.030 ug/l for PCBs.

The concentrations of all of the three metals measured were fairly high, typical of a heavily industrialized river. The particulate fraction appeared to contain a greater than expected portion of the metals for both copper and cadmium, probably due to the relatively high particulate load in this area. Copper concentrations consistently exceeded the U.S. EPA Marine Water Quality Criteria at Stations 1-3. The levels of cadmium and lead were well below the Criteria at all stations.

REFERENCES

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Table 1. PCB concentrations in whole water samples collected on 7/9/87.
Concentrations are as ug/l.

STATION	TIDE	A1242	A1254	TOTAL PCBs	MEAN
NBH-1	EBB	0.311	0.125	0.436	
NBH-1	FLD	0.865	0.217	1.080	0.758
NBH-2	EBB	0.527	0.195	0.722	
NBH-2	FLD	0.430	0.167	0.597	0.660
NBH-3	EBB	0.514	0.168	0.682	
NBH-3	FLD	0.071	0.131	0.202	0.442
NBH-4	EBB	0.056	0.052	0.108	
NBH-4	FLD	0.050	0.045	0.095	0.102

A1242 = PCB concentration measured as Aroclor 1242.

A1254 = PCB concentration measured as Aroclor 1254.

EBB = ebb tide.

FLD = flood tide.

Table 2. PCB measured in samples collected on 7/13/87. Concentrations are as ug/l.

STATION	TIDE	KIND	A1242	A1254	TOTAL PCBs	SUM	MEAN
NBH-1	EBB	PART	0.205	0.150	0.355		
NBH-1	EBB	DISS	0.612	0.151	0.763	1.12	
							0.938
NBH-1	FLD	PART	0.201	0.169	0.370		
NBH-1	FLD	DISS	0.270	0.115	0.385	0.755	
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NBH-2	EBB	PART	0.121	0.146	0.267		
NBH-2	EBB	DISS	0.355	0.109	0.464	0.731	
							0.663
NBH-2	FLD	PART	0.081	0.119	0.200		
NBH-2	FLD	DISS	0.308	0.086	0.394	0.594	
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NBH-3	EBB	PART	0.134	0.190	0.324		
NBH-3	EBB	DISS	-	-	-	-	
							-
NBH-3	FLD	PART	0.082	0.137	0.219		
NBH-3	FLD	DISS	0.262	0.138	0.400	0.619	
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NBH-4	EBB	PART	0.000	0.022	0.022		
NBH-4	EBB	DISS	0.055	0.057	0.112	0.134	
							0.125
NBH-4	FLD	PART	0.003	0.033	0.036		
NBH-4	FLD	DISS	0.054	0.026	0.080	0.116	

A1242 = PCB concentration measured as Aroclor 1242.

A1254 = PCB concentration measured as Aroclor 1254.

EBB = ebb tide.

FLD = flood tide.

PART = particulate sample.

DISS = dissolved sample.

- = sample lost.

Table 3. PCB concentrations measured at Station NBH-2 on the two sampling dates. Concentrations are as ug/l.

DATE	TIDE	KIND	A1242	A1254	TOTAL PCBs	SUM
070987	EBB	PART	0.193	0.130	0.323	
070987	EBB	DISS	0.113	0.080	0.193	0.516
070987	FLD	PART	0.133	0.137	0.270	
070987	FLD	DISS	0.309	0.098	0.407	0.677
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071387	EBB	PART	0.121	0.146	0.267	
071387	EBB	DISS	0.355	0.109	0.464	0.731
071387	FLD	PART	0.081	0.119	0.200	
071387	FLD	DISS	0.308	0.086	0.394	0.594

A1242 = PCB concentration measured as Aroclor 1242.

A1254 = PCB concentration measured as Aroclor 1254.

EBB = ebb tide.

FLD = flood tide.

PART = particulate sample.

DISS = dissolved sample.

Table 4. Whole water versus particulate and dissolved PCB measurements.
The samples were collected on 7/13/87. Concentrations are as ug/l.

STATION	TIDE	KIND	A1242	A1254	TOTAL PCBs
NBH-2	EBB	PART	0.193	0.130	0.323
NBH-2	EBB	DISS	0.113	0.080	0.193
			-----	-----	-----
			0.306	0.210	0.516
NBH-2	EBB	WWC	0.527	0.195	0.722

NBH-2	FLD	PART	0.133	0.137	0.270
NBH-2	FLD	DISS	0.309	0.098	0.407
			-----	-----	-----
			0.442	0.235	0.677
NBH-2	FLD	WWC	0.430	0.167	0.597

A1242 = PCB concentration measured as Aroclor 1242.
 A1254 = PCB concentration measured as Aroclor 1254.
 EBB = ebb tide.
 FLD = flood tide.
 PART = particulate sample.
 DISS = dissolved sample.
 WWC = whole water sample.
 - = sample lost.

Table 5. Listing of the PCB congeners that were quantified. The naming convention used is that described by Ballschmiter and Zell (1980).

CB052	-	2,2',5,5'-PCB
CB047	-	2,2',4,4'-PCB
CB101	-	2,2',4,5,5'-PCB
CB151	-	2,2',3,5,5',6-PCB
CB118	-	2,3',4,4',5-PCB
CB153	-	2,2',4,4',5,5'-PCB
CB138	-	2,2',3,4,4',5'-PCB
CB128	-	2,2',3,3',4,4'-PCB
CB180	-	2,2',3,4,4',5,5'-PCB
CB195	-	2,2',3,3',4,4',5,6-PCB
CB194	-	2,2',3,3',4,4',5,5',-PCB
CB206	-	2,2',3,3',4,4',5,5',6-PCB
CB209	-	CL10-PCB

Table 6. Concentrations of individual PCB congeners in seawater samples collected on 7/9/87. Concentrations are as ng/l.

STATION	TIDE	KIND	CB052	CB047	CB101	CB151	CB118	CB153	CB138	CB128	CB180	CB195	CB194	CB206	CB209
NBH-1	EBB	WWC	19.6	9.45	13.5	1.51	20.1	12.0	7.23	1.84	1.23	0.00	0.00	0.00	0.00
NBH-1	FLD	WWC	48.7	29.3	36.7	3.64	49.0	21.1	13.2	3.38	1.67	0.00	0.00	0.00	0.00
NBH-2	EBB	PART	17.2	9.44	17.5	2.22	17.9	12.0	7.94	2.44	1.45	0.00	0.00	0.00	0.00
NBH-2	EBB	DISS	8.10	4.29	8.45	0.00	12.2	6.69	4.63	1.22	0.00	0.00	0.00	0.00	0.00
NBH-2	EBB	WWC	35.6	20.9	31.2	3.12	40.5	17.8	11.7	3.00	1.56	0.00	0.00	0.00	0.00
NBH-2	FLD	PART	13.0	7.23	15.8	1.99	17.3	11.1	8.29	2.60	1.46	0.00	0.00	0.00	0.00
NBH-2	FLD	DISS	19.4	10.9	16.2	1.54	19.3	8.31	5.77	1.47	0.00	0.00	0.00	0.00	0.00
NBH-2	FLD	WWC	25.5	15.1	23.4	2.32	30.6	13.6	10.0	2.71	1.32	0.00	0.00	0.00	0.00
NBH-3	EBB	WWC	34.0	20.0	28.7	2.76	32.8	14.8	10.2	2.60	1.22	0.00	0.00	0.00	0.00
NBH-3	FLD	WWC	5.88	3.39	10.0	1.34	13.9	9.74	7.71	2.43	1.50	0.00	0.00	0.00	0.00
NBH-4	EBB	WWC	6.29	3.15	6.38	0.00	7.14	3.64	3.05	0.00	0.00	0.00	0.00	0.00	0.00
NBH-4	FLD	WWC	5.22	2.65	4.91	0.00	5.27	3.07	2.62	0.00	0.00	0.00	0.00	0.00	0.00

EBB = ebb tide.

FLD = flood tide.

PART = particulate sample.

DISS = dissolved sample.

WWC = whole water sample.

Table 7. Concentrations of individual PCB congeners in seawater samples collected on 7/13/87. Concentrations are as ng/l.

STATION	TIDE	KIND	CB052	CB047	CB101	CB151	CB118	CB153	CB138	CB128	CB180	CB195	CB194	CB206	CB209
NBH-1	EBB	PART	18.5	10.4	19.0	2.68	21.3	14.8	8.95	2.69	1.64	0.00	0.00	0.00	0.00
NBH-1	EBB	DISS	35.1	17.9	24.0	3.11	21.7	14.9	9.05	2.60	1.53	0.00	0.00	0.00	0.00
NBH-1	FLD	PART	17.6	10.9	20.4	2.87	22.9	15.1	10.0	3.05	1.84	0.00	0.00	0.00	0.00
NBH-1	FLD	DISS	19.2	10.4	16.7	2.16	16.8	11.4	7.23	1.96	1.12	0.00	0.00	0.00	0.00
NBH-2	EBB	PART	12.1	7.19	17.0	2.46	19.5	13.0	8.78	2.66	1.65	0.00	0.00	0.00	0.00
NBH-2	EBB	DISS	20.5	11.1	16.1	2.21	15.0	10.3	6.62	2.08	1.24	0.00	0.00	0.00	0.00
NBH-2	FLD	PART	9.03	5.54	12.5	1.84	14.5	9.47	7.20	2.41	1.54	0.00	0.00	0.00	0.00
NBH-2	FLD	DISS	18.8	9.64	14.2	1.36	11.7	7.50	5.09	1.43	0.00	0.00	0.00	0.00	0.00
NBH-3	EBB	PART	13.3	8.36	19.7	2.70	23.0	15.2	11.3	3.56	1.90	0.00	0.00	0.00	0.00
NBH-3	EBB	DISS	-												
NBH-3	FLD	PART	8.77	5.60	13.8	1.94	16.6	10.7	8.36	2.68	1.45	0.00	0.00	0.00	0.00
NBH-3	FLD	DISS	18.2	9.72	15.7	1.43	14.4	8.55	6.58	1.90	0.00	0.00	0.00	0.00	0.00
NBH-4	EBB	PART	1.95	1.11	3.27	0.00	3.86	2.98	2.47	0.00	0.00	0.00	0.00	0.00	0.00
NBH-4	EBB	DISS	4.66	2.27	4.00	0.00	3.41	2.45	1.97	0.00	0.00	0.00	0.00	0.00	0.00
NBH-4	FLD	PART	2.68	1.74	3.78	0.00	4.97	3.83	3.22	1.07	0.00	0.00	0.00	0.00	0.00
NBH-4	FLD	DISS	5.19	2.36	4.11	0.00	3.36	2.65	2.10	0.00	0.00	0.00	0.00	0.00	0.00

EBB = ebb tide.
 FLD = flood tide.
 PART = particulate sample.

DISS = dissolved sample.
 WWC = whole water sample.
 - = sample lost.

Table 8. Trace metal results for New Bedford Harbor samples collected 7/9/87.
Concentrations are as ug/l

			Cd	Pb	Cu
NBH-1	EBB	WWC	0.10	4.1	4.6
NBH-1	FLD	WWC	0.25	3.3	6.2
NBH-2	EBB	WWC	0.17	3.1	6.9
		PART	0.042	1.3	3.1
		DISS	0.14	1.2	2.8
NBH-2	FLD	WWC	0.10	2.5	9.0
		PART	0.024	1.4	4.2
		DISS	0.13	1.2	3.7
NBH-3	EBB	WWC	0.21	3.4	12.4
NBH-3	FLD	WWC	0.17	2.6	10.1
NBH-4	EBB	WWC	0.16	2.6	2.3
NBH-4	FLD	WWC	0.06	2.7	1.7

EBB = ebb tide.
FLD = flood tide.
PART = particulate sample.
DISS = dissolved sample.
WWC = whole water sample.

Table 9. Trace metal results for New Bedford Harbor samples collected on 7/13/87.
Concentrations are as ug/l

		Cd	Pb	Cu
NBH-1 EBB	WWC	0.18	3.9	7.8
	PART	0.051	1.9	3.6
	DISS	0.16	1.1	2.7
NBH-1 FLD	WWC	0.26	4.1	7.5
	PART	0.051	1.8	3.9
	DISS	0.16	1.2	3.0
NBH-2 EBB	WWC	0.19	3.4	7.3
	PART	-	-	-
	DISS	0.12	1.2	3.1
NBH-2 FLD	WWC	0.15	2.8	9.0
	PART	0.023	1.6	4.4
	DISS	0.15	1.1	3.4
NBH-3 EBB	WWC	0.15	4.2	10.8
	PART	0.029	1.6	4.2
	DISS	0.15	1.1	2.5
NBH-3 FLD	WWC	0.34	3.3	9.2
	PART	0.025	1.7	4.6
	DISS	0.19	2.0	4.6
NBH-4 EBB	WWC	0.08	2.6	2.4
	PART	0.005	0.61	0.98
	DISS	0.10	0.81	2.2
NBH-4 FLD	WWC	0.20	2.4	1.9
	PART	0.019	1.1	2.0
	DISS	0.14	1.3	2.8

EBB = ebb tide.
 FLD = flood tide.
 PART = particulate sample.
 DISS = dissolved sample.
 WWC = whole water sample.
 - = sample lost.

Figure 1. Total PCB concentrations measured at the four stations during the ebb and flood tide. (a) Whole water samples were collected on 7/9/87 and (b) the dissolved and particulate phase concentrations measured on 7/13/87. The dissolved and particulate phase concentrations were summed for this plot.

